

AD-A232 959

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1/30/91	3. REPORT TYPE AND DATES COVERED Final 6/15/87 - 8/15/90
4. TITLE AND SUBTITLE Rotational and Vibrational Spectra of Molecular Clusters			5. FUNDING NUMBERS 61102F 2303/A3
6. AUTHOR(S) Thomas R. Dyke and Joseph W. Nibler			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Oregon Oregon State University			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR- 91 0057
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Bld 410 Bolling AFB, Washington DC 20332-6448			10. SPONSORING MONITORING AGENCY REPORT NUMBER F49620-87-C-0072
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED			12b. DISTRIBUTION STATEMENT DTIC ELECTE MAR 1991 S D D
13. ABSTRACT (Maximum 200 words) <p>The principal goal of this research is to understand intermolecular forces through the structure and vibrational properties of small clusters. The intermolecular forces holding these complexes together also largely determine the properties of many important systems such as condensed phases and macromolecules. Clusters involving water are of particular interest in understanding liquid water and ice, aqueous solutions and atmospheric phenomena. Thus this work will help in understanding these systems and the general phenomena of intermolecular forces.</p> <p>Vibrational and rotational spectra of clusters produced in molecular beams were studied in this project. The tunneling-rotational spectrum of water dimer, including an unusual Coriolis resonance effect was investigated by molecular beam electric resonance spectroscopy. By similar means, the structure and internal rotation features of the $\text{NH}_3 \cdot \text{H}_2\text{S}$ complex were studied. Diode laser infrared spectroscopy was used to find vibration-rotation spectra and structural information for $\text{Ar} \cdot \text{SO}_2$, $\text{N}_2 \cdot \text{SO}_2$, $\text{Ne} \cdot \text{CS}_2$, $\text{Ar} \cdot \text{CS}_2$, $\text{Kr} \cdot \text{CS}_2$, and $\text{Xe} \cdot \text{CS}_2$. CARS techniques were used to study $(\text{CO}_2)_2$ at higher frequencies and also the "lattice" modes of larger CO_2 aggregates at frequencies below 100 cm^{-1}. Raman loss experiments were used to examine large clusters of molecular nitrogen produced in molecular beams and correlated with similar experiments on static condensed phase samples.</p>			
14. SUBJECT TERMS Hydrogen bonded molecules; van der Waals interactions; dimers; complexes; rotational spectra, infrared spectra, coherent Raman spectra			15. NUMBER OF PAGES 14
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL (UNLIMITED) SAR (SAME AS REPORT)

COMPLETED PROJECT SUMMARY

TITLE: Rotational and Vibrational Spectra of Molecular Clusters

PRINCIPAL INVESTIGATORS: Professor Thomas R. Dyke
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

Professor Joseph W. Nibler
Department of Chemistry
Oregon State University
Corvallis, Oregon 97331

INCLUSIVE DATES: 15 June 1987 - 15 August 1990

CONTRACT NUMBER: F49620-87-C-0072

COSTS AND FY SOURCE: \$170,000, FY 87; \$114,004, FY 88; \$117,646, FY 89

SENIOR RESEARCH PERSONNEL: Dr. Max Hineman Dr. John Hardwick
Dr. Andrew Lewin Dr. Michael Walsh

JUNIOR RESEARCH PERSONNEL: Mr. Rainer Beck Miss Nancy Triggs
Mr. Albert Hu Mr. Yun Der Juang
Mr. Kirk Brown

PUBLICATIONS:

"Nonlinear Raman Spectroscopy", J. Yang and J. W. Nibler, Review Chapter in "Annual Review of Physical Chemistry" Ed. by H. L. Strauss, Vol 38, 349-381 (1987), Ann. Revs. Inc, Palo Alto.

"Coherent Raman Spectroscopy of Gases", J. W. Nibler and G. A. Pubanz, Review Chapter in "Advances in Spectroscopy", Ed. by R. J. H. Clark and R. E. Hester, Vol. 15, 1-50 (1988) Wiley, London

"Photothermal Lensing Spectroscopy of Supersonic Jet Expansions of Acetylene", Rene Rodriguez, Max Hineman, and Joseph Nibler, J. Chem. Phys., 89, 2630-34, (1988).

"Vibrational Raman Spectra of Micro-Droplets and Micro-Crystals of Nitrogen Formed in Free Jet Expansions", Rainer Beck and Joseph Nibler, Chem. Phys. Lett., 148, 271-275 (1988).

"Pure Rotational Raman Loss Spectroscopy", R. Beck, K. Brown, R. Rodriguez, M. F. Hineman, M. Yang, and J. W. Nibler, pp. 165-166, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988

"Low-Frequency CARS in Free Jet Expansions", N. E. Triggs, R. Rodriguez, M. Yang, K. H. Lee, and J. W. Nibler, pp. 167-168, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988.

"Inverse Raman Spectroscopy of Micro-Droplets and Micro-Crystals of Nitrogen in Free Jet Expansions", R. Beck and J. W. Nibler, pp. 169-171, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988.

"Structure of Dicyanoacetylene as Determined by Electron Diffraction and Coherent Raman Loss Spectroscopy", K. Brown, J. W. Nibler, L. Hedberg, and K. Hedberg, J. Phys. Chem. 93, 5679 (1989).

"High Resolution Raman Loss Spectra of Solid Nitrogen and of Matrix Isolated Molecules", R. Beck and J. W. Nibler, Chem. Phys. Lett. 159, 79 (1989).

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail. and/or Special
A-1	

QUALITY
INSPECTED
3

"Coherent Raman Spectroscopy: Techniques and Recent Applications", J. W. Nibler, in "Applied Laser Spectroscopy", Eds. M. Inguscio and W. Demtroder, NATO Advanced Study Institute Series, Plenum, 1990.

"High Resolution Coherent Raman Spectroscopy", J. W. Nibler, R. D. Beck, K. W. Brown, M. F. Hineman, and N. E. Triggs, Proc. of the XII Intl. Conf. on Raman Spectroscopy, Ed. by J.R. Durig, Wiley, New York (1990).

"Stimulated Raman Probing of Supercooling and Phase Transitions in Large Nitrogen Clusters Formed in Free Jet Expansions", R. D. Beck, M. F. Hineman and J. W. Nibler, J. Chem. Phys. 92, 7068 (1990).

"Water Dimer Tunneling States With $K=0$ ", J.A. Odutola, D. Prinslow, S.E. O'dell, and T.R. Dyke, J. Chem. Phys. 88, 5352 (1988).

"Water Dimer Coriolis Resonances and Stark Effects", A. Hu and T.R. Dyke, J. Chem. Phys. 91, 7348 (1989).

"The Structure of $\text{NH}_3 \cdot \text{H}_2\text{S}$ and Free Internal Rotation Effects", P. Herbine, A. Hu, G. Johnson and T.R. Dyke, J. Phys. Chem. 93, 5485 (1990).

"Diode Laser Infrared Spectrum of the $\text{Ar} \cdot \text{SO}_2$ Complex", M.A. Walsh, A. Lewin, J. Cruzan and T.R. Dyke, to be submitted (probable journal, J. Mol. Spectrosc.).

"Vibration-Rotation Spectrum and Structure of the $\text{N}_2 \cdot \text{SO}_2$ Complex", A. Lewin, M.A. Walsh, Y.D. Juang, J. Cruzan and T.R. Dyke, to be submitted (probable journal, J. Chem. Phys.).

"Vibration-Rotation Spectrum and Structure of Rare Gas CS_2 Complexes", M. Walsh, J. Cruzan, T. Rush and T.R. Dyke, to be submitted (probable journal, J. Chem. Phys.).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The principal goal of this research is to understand intermolecular forces through the structure and vibrational properties of small clusters. The intermolecular forces holding these complexes together also largely determine the properties of many important systems such as condensed phases and macromolecules. Clusters involving water are of particular interest in understanding liquid water and ice, aqueous solutions and atmospheric phenomena. Thus this work will help in understanding these systems and the general phenomena of intermolecular forces.

Vibrational and rotational spectra of clusters produced in molecular beams were studied by microwave, diode laser infrared, and coherent Raman techniques. The tunneling-rotational spectrum of water dimer was further investigated by molecular beam electric resonance spectroscopy. An unusual Coriolis resonance was observed which explained anomalies in the relation of the rotational constants to the structure of the complex. By similar methods, microwave and radiofrequency spectra of the $\text{NH}_3 \cdot \text{H}_2\text{S}$ complex were obtained. The structure of the complex was determined through extensive deuteration studies. Although this complex is a symmetric rotor, first-order Stark effects were observed for some states, which were assigned as ammonia internal rotor states.

Diode laser infrared spectroscopy was used to find vibration-rotation spectra and structural information for a number of complexes. $\text{Ar} \cdot \text{SO}_2$ and $\text{N}_2 \cdot \text{SO}_2$ were investigated in the vicinity of the SO_2 monomer asymmetric stretching mode. Rotational constant data were obtained and some tunneling effects were seen for $\text{Ar} \cdot \text{SO}_2$. Further structural data for $\text{N}_2 \cdot \text{SO}_2$ was gained from radiofrequency and microwave spectra. $\text{Ne} \cdot \text{CS}_2$, $\text{Ar} \cdot \text{CS}_2$, $\text{Kr} \cdot \text{CS}_2$, and $\text{Xe} \cdot \text{CS}_2$ were studied near the CS_2 monomer asymmetric stretching mode and the structures of these molecules determined.

CARS techniques were used to study Raman active modes of $(\text{CO}_2)_2$. This work helped complete the picture of vibrational coupling of the monomers in this important small complex. In addition, larger CO_2 aggregates were studied at frequencies below 100 cm^{-1} . These experiments gave the first results for spectroscopic observation of "lattice" modes of a large cluster.

Raman loss experiments were used to examine large clusters of molecular nitrogen produced in molecular beams. Systematic studies of the spectra as a function of gas composition and position in the jet were carried out. These results were correlated with similar experiments on static condensed phase samples phase transitions in the isolated clusters were observed. Raman loss experiments were also done on a number of monomeric systems in free jet expansions. An interesting thermal lensing effect was observed for vibrational transitions of acetylene and water, which may prove to be a useful diagnostic for the characteristics of free jets and related gas dynamic systems.

FINAL REPORT

Rotational and Vibrational Spectra of Molecular Clusters

June 15, 1987 - August 15, 1990

**Professor Thomas R. Dyke
Department of Chemistry
University of Oregon
Eugene, Oregon 97403**

**Professor Joseph W. Nibler
Department of Chemistry
Oregon State University
Corvallis, Oregon 97331**

INCLUSIVE DATES OF REPORT: 15 March 1988 - 15 March 1989

CONTRACT NUMBER: F49620-87-C-0072

**Approved for public release;
distribution unlimited.**

OBJECTIVES OF PROJECT

Intermolecular forces manifested in hydrogen bonds and van der Waals interactions largely determine the properties of many important systems such as condensed phases and macromolecules.^{1,2} In this project, clusters produced in molecular beams are studied so that information concerning these interactions can be acquired under carefully controlled conditions. From spectroscopic measurements, precision structural data and information about the vibrational potential energy surface can be gained. These results are of great use for testing theories of intermolecular forces and for modelling the complicated systems mentioned above.

Clusters involving water are of particular interest in understanding liquid water and ice, aqueous solutions and atmospheric phenomena.^{3,5} In the latter case, various water clusters have been proposed as the species giving rise to the anomalous absorption of infrared and microwave radiation in the atmosphere.⁴⁻¹¹ That is, it is generally found that in the vicinity of water monomer atmospheric absorption lines, a broad, additional absorption is detected which is attributed to various sources such as water clusters, as mentioned above, or as the Lorentzian wings of the monomer lineshapes.¹² Our work on the rotational spectrum of $(\text{H}_2\text{O})_2$ ¹³⁻¹⁹ and the work of others²⁰⁻²⁴ shows a very complex pattern which, under pressure broadened conditions, could well produce a nearly continuous spectrum. Laboratory based measurements in the 10.4 μm infrared region have indicated that water dimers make significant contributions to atmospheric absorption below 100°C and are dominant at room temperature and below.¹¹

Vibrational and rotational spectra provide significant information for these purposes, and are the principal objectives of our project. In addition to studying systems of current interest, such as water clusters, developing and applying new infrared and coherent Raman techniques to these molecules is an important part of this work. In the long run, a balance of infrared and Raman methods should be particularly suitable for extracting a broad range of spectroscopic information for clusters. More specifically, diode laser and Fourier transform infrared methods and coherent Raman techniques such as CARS and Raman loss experiments are employed in this research.

Much of the work has been concerned with small clusters; however, some research has also been begun on larger clusters using coherent Raman techniques. Spectroscopic observations of small clusters through large clusters should give important information

concerning the structure and formation dynamics of larger aggregates, including useful diagnostics. It should yield useful insight concerning equilibrium condensed phase spectra and structure. Ultimately it should lead to a clearer picture of intermolecular forces involved in hydrogen bonding and van der Waals interactions under a variety of conditions.

CURRENT STATUS AND RESULTS OF PROJECT

Infrared and Microwave Results

Much of the recent pure rotational work at the University of Oregon has been concerned with the $(\text{H}_2\text{O})_2$ tunneling-rotational spectrum. In earlier AFOSR sponsored research, we located and assigned $K=0$ A_2^\pm/B_2^\pm transitions^{16,17} which were instrumental in unlocking the tunneling rotational transition assignment problem for this molecule and spurring much new research.¹⁸⁻²³ During this part of the project, Albert Hu made measurements on $K=1$ states of $(\text{H}_2\text{O})_2$, utilizing the molecular beam electric resonance method, which gave an important insight into the unusually wide divergence in apparent rotational constant values for different tunneling states and suggested an unusual perturbation between $K=0$ and $K=1$ rotational levels of different tunneling states. We measured microwave and radiofrequency spectra for $K = 1$ states split apart by the tunneling motion involving the interchange of hydrogen atoms on the proton acceptor water monomer of the complex. The observed rotational constants for the upper tunneling state of $K = 1$ agreed very well with those for the corresponding *lower* tunneling state for $K = 0$, while the lower $K = 1$ state was roughly 40 MHz above these values and the upper $K = 0$ state 90 MHz below. This pattern strongly suggested a rotational perturbation in which the tunneling splitting mentioned above must be approximately equal to the energy difference between the $K = 0$ and $K = 1$ states (about 7 cm^{-1}), bringing the upper $K = 0$ tunneling states into resonance with the lower $K = 1$ states; i.e. the proton donor tunneling splitting must be roughly equal the A rotational constant of about 7 cm^{-1} . These results were reported at the 1988 Columbus Molecular Spectroscopy Meeting and were in agreement with the results of far infrared work on $K = 1 \rightarrow 2$ transitions reported there by Saykally's group at Berkeley. This was then directly confirmed by $K = 0 \rightarrow 1$ A_2^\pm/B_2^\pm measurements performed by beautiful optothermal detection/electric resonance experiments by the NIST group at Gaithersburg,²³ which also gave

Table 1. Spectroscopic constants for E^\pm states (MHz).

	$E2^\pm; K=0,1$	$E1^\pm; K=1$	$E1^\pm; K=0$
$(B+C)/2$	6157.162(34)	6165.2616(8)	6160.59
$(B-C)$	78.473(36)	5.1052(14)	
D_J	0.0491(13)	[0.050] ^a	0.0467
d_1		-0.00029(2)	
ζ	1409.2(10)		
Δ	10717.(18)		

^a D_J was fixed at this value.

a detailed Coriolis perturbation analysis for those states. We have since published our results, including a deperturbation analysis for the E^\pm transitions (Table 1).¹⁹

Our initial work in the area of infrared vibrational spectroscopy was centered on SO_2 containing complexes in the ν_3 stretching region of the monomer near 1362 cm^{-1} and on CS_2 clusters near the ν_3 band origin at 1535 cm^{-1} (Figure 1,2). This work is being done with the diode laser/molecular beam spectrometer recently constructed in our lab. Michael Walsh, Andrew Lewin and Jeff Cruzan have observed spectra for argon and neon bound to SO_2 for $N_2 \cdot SO_2$, for $Ar \cdot CS_2$ and for CS_2 dimer. The rare gas complexes are undergoing interesting internal motions, which will aid in determining their vibrational potential energy surfaces. The pure rotational spectrum of $Ar \cdot SO_2$ was observed some years ago^{24,25} and exhibited a tunneling doubling of 984 MHz in the c-type transitions, while the a-type transitions showed no splitting. The vibrational transition which we observed has its transition moment oriented along the b-axis, and no apparent tunneling splitting is observed although a very small alternation in the sub-band origin frequencies is observed, which we interpret as the difference in the tunneling doubling between the ground and excited vibrational state. These "selection rules" for the tunneling splitting are consistent with a picture in which the SO_2 is tunneling in a manner similar to the ammonia inversion motion, rather than by a simple 180° rotation around its C_2 axis. The molecular constants from this work (Table 2) include the A,B, and C rotational constants and tunneling doublings for the ground and excited vibrational states.²⁶ We are currently working on accurate vibration-rotation energy level calculations to fit these results with a potential energy surface. In this work, the tunneling doublings and centrifugal distortion

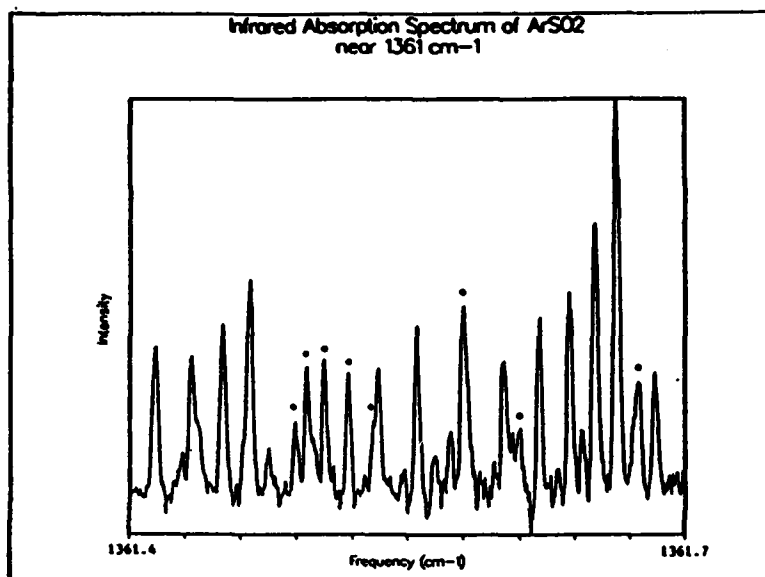


Fig. 1a Transitions for the R_{R0} and R_{Q0} branches of the Ar·SO₂ spectrum are indicated with a "." symbol. The remaining lines are high J, Q-branch transitions of SO₂ monomer.

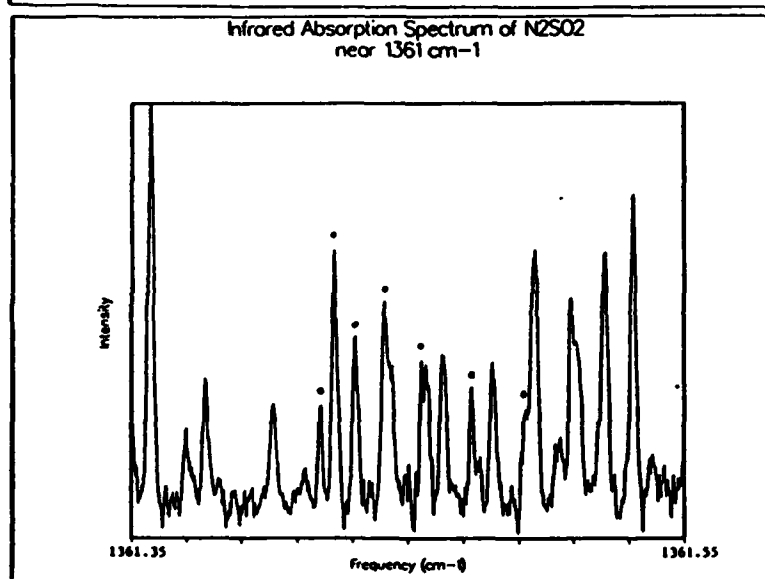


Fig. 1b R_{Q0} portion of N₂·SO₂ spectrum (indicated by ".").

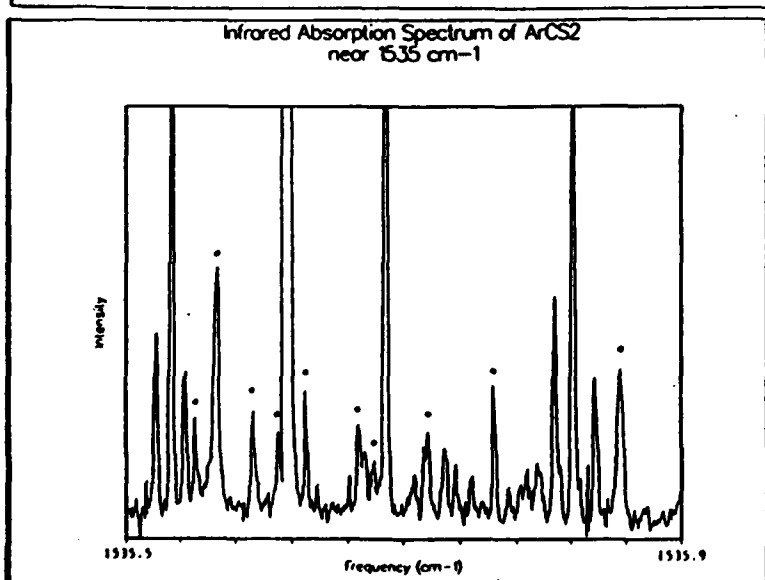


Fig. 2 Ar·CS₂ R_{Q0} and R_{R0} branches (indicated by ".").

constants will be particularly useful. We also have spectra for Ne•SO₂, which appears to be even more of a free rotor than the argon complex, although this work is still in progress.

We have also analyzed the N₂•SO₂ spectrum in this frequency region and have determined its molecular constants (Table 2). We have done a distributed multipole calculation which gives good agreement with the experimental results. We have also observed pure rotational and radiofrequency transitions for this molecule using the electric resonance spectrometer. This has allowed us to determine quadrupole coupling constants and electric dipole moments for this molecule. These latter results have been useful in complementing the rotational constant data and giving a more complete structure.²⁷

Table 2. Molecular Constants from Diode Laser Studies

	Ar•SO ₂	Ne•SO ₂	N ₂ •SO ₂	
ν_o/cm^{-1}	1361.3015(1)	-	1361.1441(2)	
$\Delta\nu_o/\text{cm}^{-1}$	-0.7592	-	-0.9166	
A"/MHz	9138.3(13)	-	8874.7(22)	
B"/MHz	1485.570(2)	2247.0(10)	1621.9(16)	
C"/MHz	1318.495(2)	2218.5(87)	1426.8(16)	
A'/MHz	9091.7(28)	-	8833.0(16)	
B'/MHz	1486.96(16)	2551.30(88)	1617.5(19)	
C'/MHz	1318.08(13)	2114.03(59)	1432.4(11)	
$\nu_{\text{tun}}^{\text{a}}/\text{MHz}$	983.8(10)			
$\nu_{\text{tun}}^{\text{b}}/\text{MHz}$	974.0(47)			
a/kHz	-381.1(14)			
D _J /kHz	11.994(64)			
D _{JK} /kHz	310.77(91)			
D _K /MHz	-2.46(32)			
d ₁ /kHz	-1.306(51)			
d ₂ /kHz	0.5845(49)			
	Ne•CS ₂	Ar•CS ₂	Kr•CS ₂	Xe•CS ₂
ν_o/cm^{-1}	1535.5372(1)	1535.4235(2)	1535.2485(2)	1535.0016(3)
$\Delta\nu_o/\text{cm}^{-1}$	+0.1804	+0.0667	-0.1083	-0.3552
A"/MHz	3312.7(21)	3294.9(10)	3295.0(84)	3288.(35)
B"/MHz	2530.2(9)	1411.9(4)	880.4(7)	664.(19)
C"/MHz	1417.9(4)	983.3(3)	692.1(1)	555.(7)
A'/MHz	3288.2(9)	3274.4(5)	3270.7(25)	3266.(16)
B'/MHz	2529.4(10)	1411.2(4)	879.5(4)	665.(15)
C'/MHz	1413.6(7)	981.1(4)	691.1(1)	554.(5)

Along this line of study, we have observed spectra for CS₂ clusters near the monomer ν_3 origin. We have currently observed and assigned the Rg•CS₂ spectra in this region (Figure 2, Table 2) for Rg = Ne, Ar, Kr and Xe. This has allowed us to obtain structural and vibrational frequency shift data for this series of rare gas complexes.²⁸ We also intend to look at a number of other complexes in the mid-infrared, including (H₂O)₂ in the monomer bending region and some work at the lowest diode laser frequencies (350 cm⁻¹) to study intermolecular modes of a number of hydrogen bonded complexes. In many instances we intend to use the molecular beam electric resonance method to complement the vibrational data with pure rotational spectroscopy, for the reasons mentioned above in connection with the SO₂ work.

Coherent Raman Results:

The initial phases of this project involved instrumental improvements to the CARS and high-resolution Raman Loss systems at Oregon State University. An injection seed laser was added to the CARS Nd-YAG laser to permit single mode operation with greatly improved linewidth and amplitude stability. This also allowed the use of a simple iodine cell optical filtering method for much better stray light rejection for low frequency rotational and vibrational studies of molecular clusters.²⁹ The scan range of the high resolution Raman Loss spectrometer was extended by the addition of a single mode krypton ion laser at 568 nm, allowing studies down to zero Raman shift at a resolution of about 0.003 cm⁻¹. Our subsequent effort focused on applications of these instruments to various problems.

CARS Studies

The CARS system was used to obtain coherent Raman jet spectra of (HCN)₂^{30,31} and (CO₂)₂³², yielding several new frequencies for the Raman active internal molecular vibrations of these small complexes. While not as revealing as rotationally resolved infrared spectra, such Raman data for IR inactive or low intensity modes aid in obtaining a more complete picture of the vibrational coupling in small prototypical clusters. Aggregate features have also been seen for expansions of H₂O and of C₂H₂ although the signal to noise was low and the size distribution was unknown. Efforts to ameliorate these problems in the study of small clusters by use of double resonance techniques and mass spectrometry are continuing.

The difficult "external" van der Waals vibrational stretching region has also been probed with some success. Jet spectra of CO_2 samples showed a weak vibrational mode at about 70 cm^{-1} with a shoulder at 90 cm^{-1} for $(\text{CO}_2)_n$ clusters. Here n is unknown but is believed to be very large (>1000 , based on similarities of the spectra with those taken concurrently for equilibrium samples of solid CO_2 films at low temperatures. This was the first case of direct spectroscopic observation of a "lattice" vibration of a large molecular cluster, an important step in probing the intermolecular interactions which govern such motions.

Raman Loss Studies

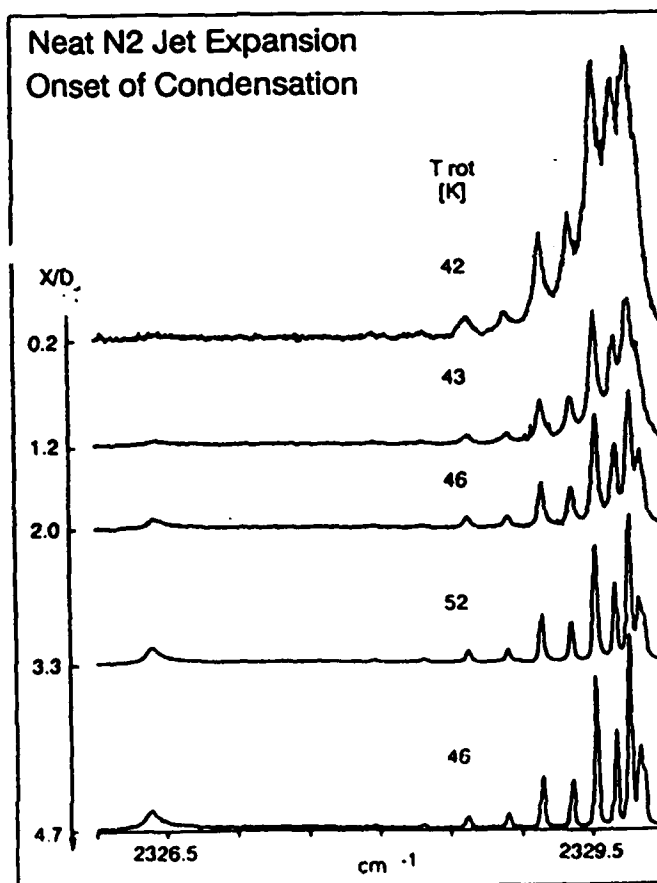
The Raman Loss instrument was used to record high-resolution spectra of static samples and of molecules cooled in free expansion jets. For example, pure rotational Raman data were obtained for dicyanoacetylene, a novel linear molecule which is quite reactive and photo-labile, so that no gas-phase structural parameters had been previously determined. This species is of interest since it is thought to exist in the atmosphere of Titan and, on earth, it is of importance as a precursor to polyacetylenes. Kirk Brown combined his Raman loss data with an electron diffraction study to determine accurate bond lengths of this species.^{33,34}

Max Hineman and Rene Rodriguez used the Raman loss apparatus to obtain jet spectra of acetylene expansions and observed a remarkable thermal lensing process which can occur in the early, high density region of the jet. This effect occurs when the Raman pump laser causes weak one-photon absorption to high overtone levels of acetylene, thereby producing a thermal lens in the early stages of a free jet expansion. This lens is detected by the cw probe beam, positioned slightly downstream in the expansion, and sharp, rotationally resolved overtone spectra of cold C_2H_2 were obtained.³⁵ A similar lensing process is seen in H_2O samples and we plan to study it further since this technique may have useful applications in determining weak one- and two-photon transition frequencies and in the study of conversion of vibrational/rotational to translational energy. The method could also serve as a useful diagnostic technique for the study of velocity, density, and temperature characteristics of flow streams over airfoils and other surfaces.

Rainer Beck used the Raman loss apparatus to study N_2 expansions and, by use of cooled channel nozzles to favor condensation, saw very large clusters evolve from early in the expansion out to and through the expansion shock front beyond 100 nozzle diame-

Figure 3

SRL spectra of N_2 expansion as a function of position in nozzle diameter units. Residual collisional broadening of the Q-branch rotational lines is seen at low X/D values. The N_2 cluster feature appears early in the expansion.



ters.^{36,37} In the 2326 cm⁻¹ region shown in Fig. 3, a cluster feature is seen whose shifts and bandwidths were correlated with accompanying measurements on static equilibrium liquid and solid samples using the same spectrometer.³⁸ This is the first use of Raman methods for the observation of a phase change in free jet clusters. The results provide a unique method of determining an average internal temperature and mean size of N₂ micro-droplets and micro-crystals. A detailed discussion of this work on N₂ is given in reference 39.

CONCLUSIONS

This research has resulted in a substantial amount of structural and vibrational data for molecular clusters, which will be useful for understanding intermolecular interactions. Our work on the water dimer system has been important for understanding this complex, which is central to modelling water-water interactions. We have helped to develop diode laser and coherent Raman techniques for studying the vibrational spectra of small and large clusters. The large cluster work provides interesting comparisons with condensed phase spectra and may be quite useful in modelling these situations.

REFERENCES

1. G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond", (Freeman, San Francisco, 1960).
2. "Water, A Comprehensive Treatise", F. Franks, ed., (Plenum, New York, 1972).
3. "Atmospheric Water Vapor", A. Deepak, T.D. Wilkerson, and L.H. Ruhnke, eds., (Academic, New York, 1980).
4. D.T. Llewellyn Jones, R.J. Knight, and H.A. Gebbie, *Nature* **274**, 876 (1978).
5. W.R. Watkins, K.O. White, L.R. Bower, and B.Z. Sojka, *Appl. Optics* **18**, 1149 (1979).
6. L.S. Bernstein, P.C. Robertson, J.A. Covant, and B.P. Sandford, *Appl. Optics* **18**, 2454 (1979).
7. H.R. Carlon, *Appl. Optics* **17**, 3192 (1978).
8. H.R. Carlon and C.A. Harden, *Appl. Optics* **19**, 1776 (1980).
9. S.H. Suck, J.L. Kassner, Jr. and Y. Yamaguchi, *Appl. Optics* **18**, 2609 (1979).
10. S.H. Suck, A.E. Wetmore, T.S. Chen, and J.L. Kassner, Jr., *Appl. Optics* **21**, 1610 (1982).
11. G.L. Loper, M.A. O'Neill, and J.A. Gelbwacks, *Appl. Optics* **22**, 3701 (1983).
12. S.A. Clough, F.X. Kneizys, R. Davis, R. Gamache, and R. Tipping, in ref. 3.
13. T.R. Dyke, *J. Chem. Phys.* **66**, 492 (1977).
14. T.R. Dyke, R.M. Mack, and J.S. Muentner, *J. Chem. Phys.* **66**, 498 (1977).

15. J.A. Odutola and T.R. Dyke, *J. Chem. Phys.* **72**, 5062 (1980).
16. Structure Determination of Weakly Bound Complexes, T.R. Dyke in "Structure and Dynamics of Weakly Bound Molecular Complexes", A. Weber, Ed. (Reidel, Dordrecht, 1987).
17. J.A. Odutola, A. Hu, D. Prinslow, S.E. O'Dell and T.R. Dyke, *J. Chem. Phys.* **88**, 5352 (1988).
18. T.A. Hu and T.R. Dyke, Forty-third symposium on Molecular Spectroscopy, Columbus, Ohio, 1988.
19. T.A. Hu and T.R. Dyke, *J. Chem. Phys.* **91**, 7348 (1989).
20. K.L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee and R.J. Saykally, *J. Chem. Phys.* **90**, 3937 (1989).
21. Z.S. Huang and R.E. Miller, *J. Chem. Phys.* **88**, 8008 (1988).
22. L.H. Coudert, F.J. Lovas, R.D. Suenram and J.T. Hougen, *J. Chem. Phys.* **87**, 6290 (1987).
23. G.T. Fraser, R.D. Suenram and L.H. Coudert, *J. Chem. Phys.* **90**, 6077 (1989).
24. R.L. DeLeon, A. Yokozeki and J.S. Muentner *J. Chem. Phys.* **73**, 2044 (1980).
25. L.H. Coudert, K. Matsumara and F.J. Lovas, Molecular Spectroscopy Symposium, Columbus Ohio, 1989.
26. M.A. Walsh, A. Lewin, J. Cruzan and T.R. Dyke, to be submitted (probable journal, *J. Mol. Spectrosc.*).
27. A. Lewin, M.A. Walsh, Y.D. Juang, J. Cruzan and T.R. Dyke, to be submitted (probable journal, *J. Chem. Phys.*)
28. M. Walsh, J. Cruzan, T. Rush and T.R. Dyke, to be submitted (probable journal, *J. Chem. Phys.*)
29. N.E. Triggs, R. Rodriguez, M. Yang, K.H. Lee, and J.W. Nibler, *Proc. of the XI Int. Conf. on Raman Spectroscopy*, pp. 167-168, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York (1988).
30. G.A. Hopkins, M. Maroncelli, J.W. Nibler, and T.R. Dyke, *Chem. Phys. Lett.* **114**, 97 (1985).
31. M. Maroncelli, G.A. Hopkins, J.W. Nibler, and T.R. Dyke, *J. Chem. Phys.* **83**, 2129 (1985).
32. G.A. Pubanz, M.P. Maroncelli and J.W. Nibler, *Chem. Phys. Lett.* **120**, 313 (1985).
33. R. Beck, K. Brown, R. Rodriguez, M. F. Hineman, M. Yang, and J. W. Nibler, "Pure Rotational Raman Loss Spectroscopy", pp. 165-166, *Proceedings of the XI International Conference on Raman Spectroscopy*, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York (1988).
34. K. Brown, J.W. Nibler, L. Hedberg, and K. Hedberg, "Structure of Dicyanoacetylene as Determined by Electron Diffraction and Coherent Raman Loss Spectroscopy", *J. Phys. Chem.* **93**, 5679 (1989).
35. R. Rodriguez, M. Hineman, and J.W. Nibler, *J. Chem. Phys.*, **89**, 2630 (1988).
36. R. Beck and J. W. Nibler, *Chem. Phys. Lett.*, **148**, 271 (1988).

37. R. Beck and J.W. Nibler, "Inverse Raman Spectroscopy of Micro-Droplets and Micro-Crystals of Nitrogen in Free Jet Expansions", pp. 169-171, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York (1988).
38. R. Beck and J.W. Nibler, Chem. Phys. Lett. 159, 79 (1989).
39. R. D. Beck, M. F. Hineman and J. W. Nibler, J. Chem. Phys. 92, 7068 (1990).

PUBLICATIONS

- "Nonlinear Raman Spectroscopy", J. Yang and J. W. Nibler, Review Chapter in "Annual Review of Physical Chemistry" Ed. by H. L. Strauss, Vol 38, 349-381 (1987), Ann. Revs. Inc, Palo Alto.
- "Coherent Raman Spectroscopy of Gases", J. W. Nibler and G. A. Pubanz, Review Chapter in "Advances in Spectroscopy", Ed. by R. J. H. Clark and R. E. Hester, Vol. 15, 1-50 (1988) Wiley, London
- "Photothermal Lensing Spectroscopy of Supersonic Jet Expansions of Acetylene", Rene Rodriguez, Max Hineman, and Joseph Nibler, J. Chem. Phys. 89, 2630-34, (1988).
- "Vibrational Raman Spectra of Micro-Droplets and Micro-Crystals of Nitrogen Formed in Free Jet Expansions", Rainer Beck and Joseph Nibler, Chem. Phys. Lett. 148, 271-275 (1988).
- "Pure Rotational Raman Loss Spectroscopy", R. Beck, K. Brown, R. Rodriguez, M. F. Hineman, M. Yang, and J. W. Nibler, pp. 165-166, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988
- "Low-Frequency CARS in Free Jet Expansions", N. E. Triggs, R. Rodriguez, M. Yang, K. H. Lee, and J. W. Nibler, pp. 167-168, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988.
- "Inverse Raman Spectroscopy of Micro-Droplets and Micro-Crystals of Nitrogen in Free Jet Expansions", R. Beck and J. W. Nibler, pp. 169-171, Proceedings of the XI International Conference on Raman Spectroscopy, Ed. by R.J.H. Clark and D. A. Long, Wiley, New York, 1988.
- "Structure of Dicyanoacetylene as Determined by Electron Diffraction and Coherent Raman Loss Spectroscopy", K. Brown, J. W. Nibler, L. Hedberg, and K. Hedberg, in press, J. Phys. Chem. 93, 5679 (1989).
- "High Resolution Raman Loss Spectra of Solid Nitrogen and of Matrix Isolated Molecules", R. Beck and J. W. Nibler, Chem. Phys. Lett. 159, 79 (1989).
- "Coherent Raman Spectroscopy: Techniques and Recent Applications", J. W. Nibler, in "Applied Laser Spectroscopy", Eds. M. Inguscio and W. Demtroder, NATO Advanced Study Institute Series, Plenum, 1990.
- "High Resolution Coherent Raman Spectroscopy", J. W. Nibler, R. D. Beck, K. W. Brown, M. F. Hineman, and N. E. Triggs, Proc. of the XII Intl. Conf. on Raman Spectroscopy, Ed. by J.R. Durig, Wiley, New York (1990).
- "Stimulated Raman Probing of Supercooling and Phase Transitions in Large Nitrogen Clusters Formed in Free Jet Expansions", R. D. Beck, M. F. Hineman and J. W. Nibler, J. Chem. Phys. 92, 7068 (1990).
- "Water Dimer Tunneling States With $K=0$ ", J.A. Odutola, D. Prinslow, S.E. O'dell, and T.R. Dyke, J. Chem. Phys. 88, 5352 (1988).

- "Water Dimer Coriolis Resonances and Stark Effects", A. Hu and T.R. Dyke, J. Chem. Phys. 91, 7348 (1989).
- "The Structure of $\text{NH}_3 \cdot \text{H}_2\text{S}$ and Free Internal Rotation Effects", P. Herbine, A. Hu, G. Johnson and T.R. Dyke, J. Phys. Chem. 93, 5485 (1990).
- "Diode Laser Infrared Spectrum of the $\text{Ar} \cdot \text{SO}_2$ Complex", M.A. Walsh, A. Lewin, J. Cruzan and T.R. Dyke, to be submitted (probable journal, J. Mol. Spectrosc.).
- "Vibration-Rotation Spectrum and Structure of the $\text{N}_2 \cdot \text{SO}_2$ Complex", A. Lewin, M.A. Walsh, Y.D. Juang, J. Cruzan and T.R. Dyke, to be submitted (probable journal, J. Chem. Phys.)
- "Vibration-Rotation Spectrum and Structure of Rare Gas CS_2 Complexes", M. Walsh, J. Cruzan, T. Rush and T.R. Dyke, to be submitted (probable journal, J. Chem. Phys.)

PERSONNEL

Oregon State University

Dr. Joseph Nibler
Dr. Max Hineman
Mr. Rainer Beck
Mr. Kirk Brown
Miss Nancy Triggs

Professor of Chemistry
Postdoctoral Fellow
Ph.D. student
Ph.D. student
Ph.D. student

University of Oregon

Dr. Thomas Dyke
Dr. John Hardwick
Dr. Andrew Lewin
Dr. Michael Walsh
Dr. Albert Hu
Mr. Yun Der Juang
Pamela Fisher
Jeff Cruzan

Professor of Chemistry
Senior Research Associate
Postdoctoral Fellow
Postdoctoral Fellow
Ph.D. (1989)
Ph.D. student
Undergraduate participant
Undergraduate participant

RECENT PRESENTATIONS AND SEMINARS RELATED TO PROJECT

T.R. Dyke

- "Vibration-Rotation Spectroscopy of Molecular Beams", University of Washington Chemistry Department, May 27, 1987.
- "Rotational and Vibrational Spectra of Molecular Clusters", AFOSR Molecular Dynamics Contractors Meeting, Newport Beach, California, October 31, 1988.
- "Observation of $(\text{H}_2\text{O})_2$ $K=1$ Transitions of E Symmetry and Discussion of Nuclear Hyperfine Splittings". Forty-Third Symposium on Molecular Spectroscopy, Ohio State University, Columbus, Ohio, June 14, 1988. A. Hu and T.R. Dyke
- "High Resolution Vibrational and Rotational Spectra of Complexes", Western Spectroscopy Association 36th Annual Conference, Asilomar, California, January 27, 1989.
- "Diode Laser Vibration-Rotation Spectroscopy of Complexes", Symposium on Structures, Properties and Dynamics of Clusters: Theory and Experiment, National ACS Meeting, Miami Beach, Florida, September 12, 1989.

J.W. Nibler

**Sept. 1989, NATO Conf. on Applied Laser Spectroscopy, two lectures "Techniques and Applications of Coherent Raman Spectroscopy"
"Coherent Raman Studies of Molecular Clusters"**

Nov. 1989, JILA Symposium, Univ. Colorado, Boulder, "Techniques and Applications of Coherent Raman Spectroscopy"

Nov. 1989, UCLA Chem. Dept. "Stimulated Raman Studies of Nitrogen Clusters"

Dec. 1990, JILA, Univ. Colorado, Boulder, "Time Domain CARS and Thermal Lensing in Jets"

Jan. 1990, JILA, P. Chem. Seminar, Univ. Colorado, Boulder, "Coherent Raman Studies of Molecular Clusters"

April 1990, Colorado State Univ., "Recent Applications of Coherent Raman Spectroscopy"

August, 1990, Plenary lecturer, XII International Raman Conference, Columbia, S.C. "High Resolution Coherent Raman Spectroscopy"

Sept. 1990, Intl. Symposium on Coherent Raman Spectroscopy, Samarkand, USSR, "Coherent Raman Spectra of Molecular Clusters and Condensed Phases"